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Multi-Use Crops and Botanochemical Production

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Scripture tells that early man recognized and used petroleum in the form of asphalts, tars, and oils. Coal gained acceptance in the 16th century, and its use continued to expand into the 20th century. However, before the petroleum industry began to take shape in the mid-19th century and virtually exploded onto the industrial scene with invention of the internal combustion engine, man relied principally on renewable materials for his energy, oil, and hydrocarbon resources. Today, with the decline in readily removable petroleum and rising costs of liquid fuels and chemical feedstocks, man is developing a renewed awareness of the potential value of underutilized and diverse plant species.

Numerous investigators have advanced ideas for development of energy and chemical resources from plants. The energy plantation has been analyzed in detail by Szego and Kemp (1) and Goldstein (2). Concepts of "petrol plantations" have been described by Calvin (3,4), and companies such as Diamond Shamrock (5) and Goodyear (6) are investigating their potential. "Integrated idaptive agricultural systems" have been discussed by Lipinsky (7), and luchanan and Otey have advanced their "multi-use botanochemical ystems" (8). In all of these proposals, entire above-ground material is to be arvested and used. And, in the most advanced schemes, fuel and chemical edstock production is integrated with production of food and feed.

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If fuel is to become a major farm product, new agricultural practices and systems should maximize energy product per unit energy input. Low-energy crop production and energy-efficient processing methods and handling techniques must be components for future agricultural scenarios. Such a scheme has been proposed by Buchanan and Otey (8).

BOTANOCHEMICAL SCREENING

The plant kingdom provides a reservoir of 250,000 to 300,000 known plant species. Fewer than 0.1% have enjoyed any significant commercial recognition in the world. From this wealth of plant resources, we anticipate that new sources of energy-producing plants could be identified and exploited.

Oil- and hydrocarbon-producing plants are especially attractive as future energy and chemical resources. Plants already supply several products competitive with synthetic petrochemicals. These products include tall oil, naval stores, seed oils, and plant oils. For this discussion, we refer to such products collectively as oils and hydrocarbons.

For many years, the U.S. Department of Agriculture has actively pursued a multi-disciplined approach to identify and establish new crops as renewable resources (9). Patterned after the Department's program to identify annually renewable fibrous plants that could be cultivated for papermaking (10), an analytical screening program was instituted in 1974 to identify and evaluate species as sources of multi-use oil- and hydrocarbon-producing crops for food material and energy production (11,12). The multi-use concept requires plant breeders and agronomists to deal with a variety of new crops, each yielding several different products of varying economic value. In screening plant species as potential corps, a rating system was employed that emphasized potential economy of plant production, total biomass yield, and oil and hydrocarbon content (8). Subsequently, all candidates were ranked by this rating system. It should be emphasized that vigorous perennials were given preference over annuals, with the concept that seed-bed preparation would be infrequent for perennials.

Data for over 300 species have been accumulated, and about 40 species have been identified that have sufficient potential to merit further consideration. Nearly all of these species are being further investigated by USDA plant scientists; meanwhile, the screening program continues.

In the original scenario, potential rubber crops were considered. Since then, it was decided to develop guayule (*Parthenium argentatum*) as a domestic source for natural rubber (13). The U.S. rubber market can potentially be supplied by guayule grown in the southwest. Thus, barring discovery of an

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exceptional candidate, that decision preempts development of other rubber crops. However, several potential botanochemical crop species produce low-molecular-weight soluble rubbers (14) that would be valuable as a hydrocarbon component of whole-plant oils.

Our analytical procedure consists of stepwise acetone extraction followed by cyclohexane. Subsequently, the acetone-soluble fraction is partioned between hexane/aqueous ethanol (12.15), and the soluble components are freed of solvents and determined gravimetrically. For lack of specific nomenclature, the botanochemicals isolated by this technique have been referred to as "whole plant oil," "polyphenol," and "polymeric hydrocarbon." Actually, components from these extracts need to be further characterized. However, petroleum refinery processes may be sufficiently insensitive to allow use of carbon-hydrogen rich compounds represented by a broad spectrum of structures. For example, consider the diverse chemicals ranging from methanol to natural rubber which have been converted to gasoline (16). Thus, chemical species may be important if chemical intermediates are being generated but may be nonconsequential for production of fuels, solvents, carbon black, and other basic chemicals.

PROMISING SPECIES FOR WHOLE PLANT USE

Plant families from which more than one promising species has been identified thus far are Anacardiaceae, Asclepiadaceae, Coprifoliaceae, Compositae, Euphorbiaceae, and Labiatae. However, representative species from ten other families have been identified as having sufficient potential to merit further consideration. Undoubtedly, the sample base is too incomplete to establish any trends.

Crop ratings and proximate composition of promising species are summarized in Table I. Species containing the greater amount of oil, all exceeding 6%, were Ambrosia trifida, Campanula americana, Asclepias hirtella, and the three Euphorbiaceae. Those with the most abundant polymeric hydrocarbon, exceeding 2%, were Asclepias subulata, A. tuberosa, Crystostegia grandiflora, Cacalia atriplicifolia, Parthenium argentatum. Elaegnus multiflora, and Agropyron repens. Seven species had more than 15% of the polar fraction labelled polyphenol, i.e., Acer saccharinum, Rhus glabra, Lonicera tatarica, Elaeagnus multiflora, Xylococcus bicolor. Teucrium canadensis, and Prunus americanus. And one species, Vernonia altissima, had more than 0% of apparent protein.

otein contents are calculated from Kjeldahl nitrogen values by annihitor 6.25 as the nitrogen equivalent for protein the cogenous components must be officer.

sion of leafy plants as protein resources, Kohler *et al.* remind us that in addition to desirable nutrients, most plants contain compounds which, if not appropriately dealt with, may be deleterious to animals (17). They also discuss several processing schemes which may provide insights into processing plants identified during the screening program.

PLANT OIL AND HYDROCARBON-PRODUCING SPECIES

During World War II. Parthenium argentatum, Cryptostegia grandiflora, Crysothamnus nauseosus, and Solidago leavenworthii were given considerable attention as possible domestic rubber sources (18). P. argentatum is undergoing vigorous reinvestigation (19). Taraxacum kok-sagbyz (Russian dandelion), although not listed in Table I principally because of botanical characteristics, was also a strong candidate as a potential rubber crop during the 1940's (20). See Table II for comparisons of Hevea brasiliensis rubber molecular weights with those of species identified by Swanson, Buchanan, and Otey (14).

Relatively few plant species have been proposed as potential U.S. oil and hydrocarbon crops. As previously stated, there is considerable current interest in guayule for production of natural rubber. Rubber is a pure hydrocarbon easily depolymerized into isoprene or reformed into gasoline (16). For this use, low molecular weight may be an advantage; the polyisoprene probably is best extracted as a hydrocarbon component of a whole-plant oil. A milkweed, *Asclepias speciosa*, is being grown experimentally in Utah. USDA agronomists are studying the common milkweed, *Asclepias syriaca*, and a few rubber- and oil-producing species in other plant families.

Gutta has been found in several Gramineae species (21). Although these species are low in combined oil and hydrocarbon content. *Elymus canadensis* is being grown in small plots to test its response to plant growth stimulants, and the genetic variability of *Agropyron repens* is being evaluated.

A few Euphorbiaceae have been suggested as crops for production of a whole-plant oil low in polyisoprene content. Calvin has drawn particular attention to Euphorbia lathyrus and Euphorbia tirucalli, species that are accustomed to arid lands, and has suggested that Asclepiadaceae and Euphorbiaceae deserve increased attention because they generally contained—and hydrocarbon-rich latexes. Hexane-extractable material from

Thu/lb (22). This material consists almost ent

		Crude	Polyphenol	Oil	Polymeric	_	
Family-Genus-Species	Common Name	Protoin, %	Fraction,	Fraction, %	Hydrocarbons %	Type ^b	op Rating
Aceraceae							
Acer saccharinum	Silver maple	16.3	198	24	0.39	***	9
Anacardiaceae							
Rhus glabra	Smooth sumac	7.1	20.2	5.9	0.21	W	10
Rhus faurina	Laurel sumac	8.1	10.5	5.5	1 44	W	8
Apocynaceae							
Apocynum							
androsaemitolium	Spreading dogbane	17.0	7.8	30	0.50	R.W	10
Asclepiadaceae							
Asclepias hirtella	Green milkweed	14.2	4.4	77	0 49	R	10
Asclepias incarnata	Swamp milkweed	11.0	11.5	30	1.87	Я	10
Asciepias subulata	Desert milkweed		Andre	114°d	2 95°	R	8
Asclepias syriaca	Common milkweed	12.3	80	48	1 54	R	9
Asclepias tuberosa	Butterfly-weed	8.1	12.3	3.1	2 84	A	9
Cryptostegia grandiflora aprifoliaceae	Madagascar rubber vine			67 ^{c a}	2 19 ^c	R	10
Lonicera tatarica	Red tatarion honeysuckle	10.2	15.8	34	1 77	R	9
Sambucus canadensis Symphoricarpos	Common elder	6.5	6.6	2.2	0.52	A	10
orbiculatus	Coral berry	5.9	11.1	23	0.81	R	10
riosteum perfoliatum panulaceae	Tinker's weed '	7.1	14.2	2.6	1.43	Я	10
mpanula americana	Tall bellllower	9.7	62	65	0 99	R.W	10

Table 1. COMPOSITION AND CROP RATING OF REPRESENTATIVE BOTANOCHEMICAL-PRODUCING SPECIES*

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Compositae							
Ambrosia trifida	Giant ragweed	11.4	44	83	0 60	R	10
Cacalia atriplicifolia	Pale Indian-plantain	11.7	9 4	34	3 46	R	8
Chrysothamnus nauseosus	Rabbitbrush	-		115 ^{c d}	167°	R	8
Cirsium discolor	Field thistle	5.9	3.9	58	0 40	R.W	10
Eupatorium aitissimum	Tall boneset	86	10.8	59	0 5 6	R.W	10
Helianthus							
grosseserratus	Cut-leaf sunflower	8.8	92	23	0 76	R	10
Parthenium agentatum	Guayule	18.1	7.7	4 4	4 98	R	10
Rudbeckia subtomentosa	Sweet coneflower	5 9°	7 8°	2 40	1 22 ^e	A	10
Silphium integrifolium	Rosin weed	62	70	28	0.79	R	10
Silphium laciniatum	Compass plant	98	81	33	0 75	A	10
Silphium							
terbinthinaceum	Prairie dock	4.5	63	28	0 94	R	10
Solidago graminifolia	Grass-leaved goldenrod	5.6	134	26	151	R	10
Solidago leavenworthii	Edison's goldenrod	129	89	50	1 52	R	8
Solidago ohioensis	Ohio goldenrod	6.8	86	25	0 5 4	A	10
Solidago rigida	Stiff goldenrod	4.9	68	24	1 48	R	10
Sonchus arvensis	Sow thistle	9 3°	11.0	5 3°	0 72°	R.W	10
Veronia altissima	Tall ironweed	21.6	69	3 1	0.38	spike e	10
Veronica fasciculata	fronweed	11.4	8.4	5 4	0 39	R	10
Elaeagnaceae .							
Elaegnus multiflora	Cherry elaeagnus	11.9	18.9	23	2 03	R	10
Ericaceae							
Xylococus bicolor	_	7.2	186	5 4	1 08	R	10
Elymus canadensis	Canada wildrye	7.0	5.5	1.7	1 35	G	11

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Table I. COMPOSITION AND CROP RATING OF REPRESENTATIVE BOTANOCHEMICAL-PRODUCING SPECIES® (Continued)

		Crude Protein.	Polyphenol Fraction.	Oil Fraction.	Polymeric Hydrocarbons	C	тор
Family-Genus-Species	Common Name	%	%	%	%	Typeb	
Euphorbiaceae							
Euphorbia dentata	Cut-leaf spurge	19.4	4.1	11.2	0 20		
Euphorbia lathyris	Mole plant	12.7	7.6	9.9	0.40		9
Euphorbia pulcherrima	Poinsettia	16.4	6.4	63	0 66	W	10
Gramineae							
Agropyron repens	Quackgrass	12.2	4.6	2.4	1.95	G	10
Labiatae							
Pycnanthemum incanum	Mountain mint	13.3	80	2 2	1 36	R	10
Teucrium canadensis	American germander	14.3	16.7	2 7	1 44	R	10
Lauraceae							
Sassafras albidum	Sassafras	89	144	5.7	0 23	W	10
Phytolaccaceae							
Phytolacca americana	Pokeweed,	15.5°	5.9°	3 4"	0 17 ^e		10
Rhamnaceae							
Ceanothus americanus	New Jersey tea	124	12.8	3.4	0 67	W	10
Rosaceae							
Prunus americanus	Wild plum	17.3	18.5	46	0 20	***	10

^a Values are moisture and ash free, crude protein is calculated from Kjeldahl nitrogen with the factor 6.25

b Identified by infrared G - gutta, R - rubber, W - wax.

c Literature values.

d Also contains Polyphenol fraction.

Values are moisture free but are not corrected for ash.

Centaurea vochinesis Bernh.

Table II. MOLECULAR WEIGHT OF NATURAL RUBBERS RELATIVE TO HEVEA BRASILIENSIS RUBBER

Species	Common Name	Ratio
Hevea brasiliensis Mull arg.	Rubber tree	1 00
Parthenium argentatum A Gray	Guayule	0.98
Pycnanthemum incanum (L.) Michx	Mountain mint	0.38
Lamiastrum galeobdolon (L.) Ehrend and Polatsch	Yellow archangel	0.32
Monarda fistulosa L.	Wild bergamont	0.32
Veronia fasciculata Michx.	Ironweed	0.32
Symphoricarpos orbiculatus Moench	Coral berry	0.28
Sonchus arvensis L.	Sow thistle	0.25
Xylcoccus bicolor Nutt.	Two-color woodberry	0.25
Melissa officinalis L.	Balm	0.24
Silphium integrifolium Michx.	Rosinweed	0.22
Helianthus hirsutus Raf.	Hirsute sunflower	0.21
Cirsium vulgare (Savy) Ten.	Bull thistle	0.20
Cacalia atriplicifolia.L.	Pale Indian plantain	0.20
Euphorbia glyptosperma Engelm.	Ridgeseed Euphorbia	0.20
Monarda didyma L.	Oswega tea	0.20
Lonicera tatarica	Tartarian honeysuckle	0.19
Triosteum perfoliatum L.	Tinker's weed	0.18
Solidago altissima L.	Tall goldenrod	0.18
Cirsium discolor (Muhl.) Spreng.	Field thistle	0.18
Solidago gramınıfolia (L.) Salisb.	Grass-leafed goldenrod	0.18
Apocynum cannabinum L.	Indian hemp	0.16
Polymnia canadensis L	Leafy cup	0.16
Gnalphalium obtusifolium L.	Fragrant cudweed	0.16
Silphium terebinthinaceum Jacq	Prairie dock	0.15
Euphorbia pulcherrima	Poinsettia	0.15
Asclepias incarnata L.	Swamp milkweed	0.14
Grindelia squarrosa (Pursh.) Duval.	Tarweed	0.13
Veronia altissima Nutt.	Ironweed	0.13
Solidago rigida L.	Stiff goldenrod	0.12
Euphorbia corollata L.	Flowering spurge	0.12
Helianthus grossesserratus Martens	Sawtooth sunflower	0.12
Elaegnus multiflora Thunb.	Cherry Elaegnus	0.12
Rudbeckia laciniata L.	Sweet coneflower	0.12
Pycnathemum virginianum (L.) Durand & Jackson	Mountain mint	0.11
Campsis radicans (L.) Seem, ex Bur.	Trumpet creeper	0.11
Chenopodium album L.	Lambsquarter	0.11
Monarda punctata L.	Horsemint	0.11
Apocynum androsaemifolium L.	Spreading dogbane	0.11
Asclepias tuberosa L.	Butterfly weed	0.10
Nepeta cataria L.	Catnip	0.10
Teucrium canadense L.	American germander	0.10
Solidago ohioensis Riddell	Ohio goldenrod	0.10
Artemisia vulgaris L.	Common mugwort	0.10
Aster laevis L.	Smooth aster	0.10
Asclepias syriaca L.	Common milkweed	0.09
Artemisia abrotanum L.	Southernwood	0.09
Campanula americana L.	Tall bellflower	0.09
	and the second s	

Knapweed

80.0

Table II. MOLECULAR WEIGHT OF NATURAL RUBBERS RELATIVE TO HEVEA BRASILIENSIS RUBBER

(Continued)

Physostegia virginiana (L.) Benth.	Obedient plant	0.08
Verbena urticifolia L.	White vervain	0.08
Euphorbia cyparissias L.	Cypress spurge	0.08
Ocimum basilicum L.	Purple basil	0.08
Asclepias hirtella (Pennell Woodson)	Milkweed	0.08
Achillea millefolium L	Yarrow	0.07
Phyla lanceolata (Michx) Greene	Frog fruit	0.07
Gaura biennis L	Gaura	0.07

of polycyclic triterpenoids. *E. lathyris* is being further evaluated at the University of Arizona (<u>5)</u>, and USDA is evaluating *E. pulcherrima* and several other Euphorbiaceae.

During the summer of 1979, USDA made a special effort to collect Leguminosae species. And in September 1979, Calvin drew attention to the Leguminosae *Copaifera langsdorfii* which, he observed, produces virtually pure diesel fuel (23).

POLYPHENOLS AND TANNINS

The rather simple solvent classification schemes yield complex fractions of botanochemicals. Their detailed composition depends not only on the species but also on maturity of the plant and the method of extraction (15.22). The polar fraction isolated by acetone extraction and readily soluble in 87.5% aqueous ethanol, termed "polyphenol" by Buchanan and coworkers (11.12), no doubt consists of phenolics and a wide variety of other substances. For plants of high tannin content, (e.g., *Rhus głaubra*) the polyphenol fraction might well be called tannin.(24)

HARVESTING AND PROCESSING SCHEMES

Harvesting and processing technologies will need to be developed and individually tailored to each species. A multi-disciplined approach is essential to capture the full potential offered by the various species. While it is beyond the scope of this review to elaborate on the many facets, major areas of concern are: harvesting method and timing, handling, storage, and separation and recovery of materials. For example, see some USDA experiences with the development of promising new crops crambe and kenaf (25,26).

Processing of whole plant materials for oil and hydrocarbon has been discussed by Buchanan and Otey (8) and Nivert and coworkers (27). In the process envisioned, baled plant material is flaked in equipment common to the soybean processing industry. The flakes are subsequently extracted by the appropriate solvent, perhaps by a sequential extraction using several solvents.

LIGNOCELLULOSIC RESIDUE

In all plant materials, the major component will be the cellular lignocellulosic material. Several possible uses for this material exist. Some of the more attractive are cattle feed; fiber for pulp, paper, and board; chemical feedstock; or energy (8,11,12). Detailed evaluation of the cellular portion should provide bases for suggesting their most appropriate uses.

CONCLUSIONS

Green plants are solar-powered chemical factories that convert carbon dioxide and water into a variety of energy-rich compounds. Crops can be developed to help provide renewable sources of fuels and chemicals and at the same time to provide a continuing source of feed and food. Several candidates have been identified, which can become future crops for American Agriculture.

REFERENCES

- Szego, G. C.; Kemp, C. C. Chemtech 1973, 275.
- 2. Goldstein, I.S. Chem. Eng. News 1976, 54, 4.
- 3. Calvin, M. Rubber World 1974, 170, 16.
- 4. Calvin, M. BioScience 1979, 29, 533.
- 5. Diamond Shamrock Co. Chem. Eng. News 1978, 56, 21.
- 6. Goodyear Tire and Rubber Co. Rubber World 1979, 179, 21.
- 7. Lipinsky, E. C. Science 1978, 199, 644.
- 8. Buchanan, R. A.; Otey, F. H. Biosources Dig. 1979, 1, 176.
- 9. Wolff, I. A.; Jones, Q. Chem. Dig. 1958, 17, 4.
- Nieschlag, H.J.; Nelson, G. H., Wolff, I. A.; Perdue, R. E., Jr. *Tappi* 1960.
 43, 193.
- Buchanan, R. A.; Cull, I. M.; Otey, F. H.; Russell, C. R. Econ. Bot. 1978, 32, 131.
- Buchanan, R. A.; Cull, I. M.; Otey, F. H.; Russell, C. R. Econ. Bot. 1978, 32, 146.
- 13. 95th U.S. Congress, 1978, Public Law 95-592,
- Swanson, C. L.; Buchanan, R. A.; Otey, F. H. J. Appl. Polym. Sci. 1979, 23, 743.

- Buchanan, R. A., Otey, F. H., Russell, C. R., Cull, I. M. J. Am. Oil Chem. Soc. 1978, 55, 657
- 16. Weisz, P. B., Haag, W. O., Rodewald, P. G. Science 1979, 206, 57.
- 17. Milner, M.; Scrimshaw, N. S.; Wang, D. I. C., Ed. "Protein Resources and Technology: Status and Research Needs"; Avi Publishing Co.: Westport, Conn., 1978; p 543.
- 18. Trumbull, H. L. Ind. Eng. Chem. 1942, 34, 1328.
- McGinnies, W. G.; Haase, E. F., Ed. "An International Conference on the Utilization of Guayule," Proceedings of Meeting held at Tucson, Arizona, November 1975.
- Whaley, W. K.; Bowen, J. S., "Russian Dandelion, An Emergency Source of Natural Rubber," U.S. Department of Agriculture No. 618, 1947.
- Buchanan, R. A.; Swanson, C. L.; Weisleder, D.; Cull, I. M. *Phytochemistry* 1979 18, 1069.
- Nemethy, E. K.; Otvos, J. W.; Calvin, M. J. Am. Oil chem. Soc. 1979, 56, 957.
- 23. Calvin, M. (Thomas H. Maugh II) Science 1979, 206, 436.
- Clarke, I. D.; Rogers, J. S.; Sievers, A. F.; Hopp, H. "Tannin Content and Other Characteristics of Native Sumac in Relation to Its Value as a Commercial Source of Tannin"; U.S. Department of Agriculture, No. 986, 1949.
- Princen, L. H. "Potential Wealth in New Crops: Research and Development", in "Crops Resources". Academic Press: New York, 1977.
- Bagby, M. O. "Kenaf: A Practical Fiber Resource". Atlanta. Ga., TAPPI Press Reports Nonwood Plant Fiber Pulping Progress Report No. 8, 1977.
- 27. Nivert, J. J.; Glymph, E. M.; Snyder, C. E. "Preliminary Economic Analysis of Guayule Rubber Production", 2nd International Guayule Conference, Saltillo, Coahuila, Mexico, Aug. 1977.